

# ***PROCEEDINGS***

## ***TWENTY-THIRD ASILOMAR CONFERENCE ON POLYMERIC MATERIALS***

*February 6-9, 2000*

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## REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) At the 2000 Asilomar Conference on Polymeric Materials, emphasis was on tunable properties in polymeric materials. The conference included such topics as tunable optical polymers, assembly of intelligent molecules, biomolecular recognition of semiconductor and magnetic systems, smart surfaces, and molecular machines. Both synthetic polymeric materials and biological systems were considered. Special emphasis was on such issues as the integration with inorganic, polymeric, and biological compounds. As in previous years, this conference addressed the problems and opportunities that are arising with the emergence of an hierarchical approach to the design of new materials systems. This conference also focused on the newly emerging tunable systems. The Twenty-Third Asilomar Conference was organized along multidisciplinary lines in order to accommodate the perceived needs for the translation of the existing knowledge between disciplines. Since this conference addressed the most advanced polymeric systems of today, selected examples from other disciplines including naturally occurring organic and inorganic systems were chosen.				
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*Program*

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*Twenty-Third Asilomar Conference  
on Polymeric Materials*

*February 6-9, 2000*

*Pacific, Grove, CA*

**ATTENDEES LIST**  
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**ON POLYMERIC MATERIALS**

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*Abstracts*

*Asilomar Conference*



*Twenty-Third Asilomar Conference  
on Polymeric Materials*

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## **Amplification of Biospecific Interactions at Surfaces Using Liquid Crystals**

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Anisotropic interactions between thermotropic liquid crystals and surfaces typically cause liquid crystals to be "anchored" in one or more orientations near surfaces. Past interest in the anchoring of liquid crystals near surfaces has revolved around the design of surfaces that uniformly orient liquid crystals over large areas, as needed for flat panel displays. Reliable and economical methods based on the mechanical rubbing of polymer films have now largely satisfied this technological need. In this talk, we report an investigation of a possible new use for surface anchoring phenomena involving liquid crystals: the imaging of biomolecular recognition events at surface. The approach is based on the observation that anisotropic forces acting between a liquid crystal and an appropriately designed surface can be perturbed by the formation of biological complexes on the surface. The change in structure of the liquid crystal near the surface is communicated deep into the bulk liquid crystal because the orientational correlation lengths of liquid crystals are typically large (micrometers). We report the design of spontaneously organized surfaces so that protein molecules, upon binding to ligands hosted on these surfaces, trigger changes in the orientations of 1-20 micrometer-thick films of supported liquid crystals, thus corresponding to a reorientation of  $\sim 10^5$ - $10^6$  mesogens per protein. Binding-induced changes in the intensity of light transmitted through the liquid crystal are easily seen with the naked eye and can be further amplified by using surfaces designed so that protein-ligand recognition causes twisted nematic liquid crystals to untwist. We also use the average gray-scale brightness of the optical appearance of the supported liquid crystal to construct an optical response curve as a function of the amount of bound protein. This approach to detection of ligand-receptor binding does not require labeling of the analyte, does not require the use of electroanalytical apparatus, provides a spatial resolution of micrometers, and is sufficiently simple that it may find use in biochemical assays and imaging of spatially-resolved chemical libraries.



# Polymeric Metal Complexes by Metalloinitiator and Macroligand Chelation Strategies

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## Introduction

The combination of inorganic chemistry with controlled polymerization allows for the synthesis of metal complexes with monodisperse macroligands. These materials resemble metalloproteins in that single metal complexes are embedded in well-defined polymeric environments. Many features of these site-isolated metal-centered polymeric systems are tunable including the ligand sets, metal ions, counterions, oxidation states, polymer composition, molecular weights, architectures and chain termini. This makes them well suited for use as materials that respond to heat, light, reagents, electrical, magnetic, and mechanical stimuli. Moreover, the aggregation behavior of block copolymer analogues leads to metal-containing nanopatterned films, whereas reactive systems could serve as catalysts. We are currently exploring applications for these materials in biomedical contexts.

## Discussion

The development of synthetic routes to metal complexes with macroligands and the systematic exploration of the scope of this concept have served as the focus of our efforts thus far. Linear and star-shaped homopolymers and block copolymers with tailored metal binding sites are readily prepared using divergent metalloinitiator or convergent metal template strategies (Figures 1 and 2). New and efficient syntheses of halomethyl and hydroxymethyl bipyridines and their metal complexes have made it possible to demonstrate that these reagents are compatible with a wide range of controlled and living polymerization methodologies.

Functionalized metalloinitiators have been utilized to generate metal centered polyoxazolines, both homopolymers as well as star block copolymers. Labile iron-centered polymers exhibit interesting sensitivity to heat, reagents, and mechanical shear as evidenced by their fragmentation during GPC analysis. Inert Ru tris(bipyridine) and related  $\alpha$ -diimine derivatives luminesce as expected. Related polystyrene, poly(methyl acrylate) and poly(methyl methacrylate) materials have been prepared in an analogous manner using suitably functionalized halide initiators and standard ATRP methodologies. In some cases, the metalloreagents enhance the control that is observed in the polymerization reaction, whereas in others it appears

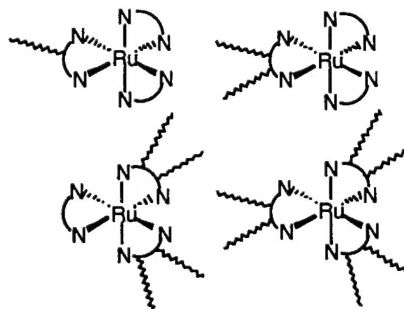


Figure 1. Representative dicationic Ru-centered polymers with one, two and three macroligands.

to compromise it to some extent, depending on the specific ATRP catalyst and monomer.

An alternate approach to polymeric metal complexes involves the chelation of metal ions to narrow dispersity polymers with tailored binding sites. This metal template approach offers a very interesting and versatile route to a wide range of polymer architectures. Issues of compatibility of metalloreagents and controlled polymerization are circumvented. By varying the ancillary ligands in heteroleptic complexes, the properties and functionalities at the core may be varied. Moreover, chelation of different kinds of macroligands results in block copolymers or heteroarm stars, with the metal serving as a well defined, tunable crosslink. Features that are important in the extension of coordination chemistry to polymeric ligands, such as solvent polarity and the importance of dehalogenating metal complex intermediates will be discussed.

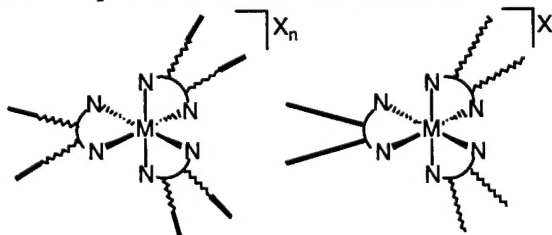


Figure 2. Metal centered block copolymers.

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## Intermolecular Interactions in Electro-Optic Polymers

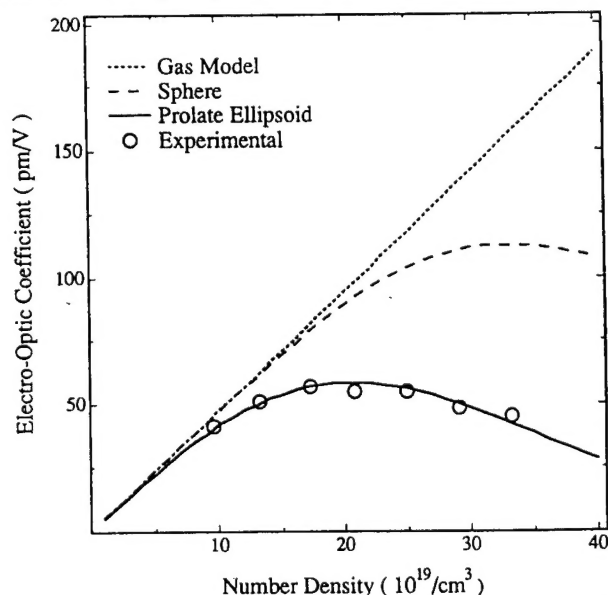
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Electro-optic polymers can be used to transduce electrical signals into optical signals, and to switch optical signals between waveguides in an optical network. Typical electro-optic polymers are characterized by second-order nonlinear optical (NLO) chromophores arranged polar-asymmetrically in an amorphous polymer matrix. It is believed that the electro-optic activities of traditional NLO chromophores are of insufficient magnitude to be viable candidates for commercial device-quality materials. Consequently, much effort has been directed in the past few years toward the development of chromophores with device-quality magnitudes of molecular optical nonlinearities. However, the translation of these new NLO chromophores to the expected bulk electro-optic activities generally has not been achieved. Recently, we have shown that this lack of electro-optic activity is due primarily to strong intermolecular electrostatic interactions between chromophores, which tend to align the chromophores in an antiparallel fashion. This results in little or no net polar asymmetry in the bulk material, and hence the low observed electro-optic activities.

Reformulation of the equilibrium statistical mechanical models used to describe polar order, to include inter-chromophore electrostatic interactions, accurately predicts the electro-optic behavior of polymers containing these new-generation chromophores. Figure 1 shows a comparison of theory to experiment for one such electro-optic polymer.

**Figure 1.** Comparison of experimental electro-optic coefficient data for composite samples of FTC in PMMA with results of various theoretical models. The dotted line corresponds to the neglect of intermolecular electrostatic interactions (an ideal gas model). The dashed line represents full treatment of intermolecular electrostatic interactions but approximates the chromophore shape as a sphere. The solid line represents full treatment of intermolecular electrostatic interactions but treats chromophores as prolate ellipsoids.



Characterization of the various electrostatic intermolecular interactions in NLO chromophores will be discussed. Details of these equilibrium statistical mechanical approaches, as well as a recent Monte Carlo treatment will be given. These models have guided synthetic efforts aimed at circumventing these interactions in electro-optic polymers, and have led to device-quality electro-optic activities. Current work along these lines will be discussed as well.

## **Tunable Optical Polymer Materials and Devices**

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Polymeric materials having optical properties that are tunable in real time are promising for many photonic and optoelectronic applications ranging from large area information displays, smart sensors/detectors, photoresponsive transducers, and information storage to large area color-tunable wallpapers or coatings. Electrochromism, photochromism, and thermochromism are some examples of current optical tunability in polymers. To explore new concepts of tunable optical properties and new generations of chromogenic polymers the Army recently funded a multidisciplinary university research initiative program on Tunable Optical Polymer Systems (TOPS). We are exploring absorption, emission, and/or reflection switching in polymeric materials. In my talk I will focus primarily on one area: tunable multicolor electroluminescence from nanostructured multicomponent conjugated polymer systems. Simple bilayer polymer/polymer heterojunction light emitting diodes of suitable composition and layer thicknesses have been found to exhibit continuous voltage tunability of emission colors throughout the CIE color space. Such a voltage tunable multicolor emission is exemplified by red (5V)  $\leftrightarrow$  yellow (9V)  $\leftrightarrow$  green (12 V) and other intermediate color switching in poly(p-phenylene vinyene)/poly(phenylquinoline) diodes. Charge transfer at the polymer/polymer interface and finite size effects were found to control the emission tunability and performance of light-emitting devices based on multicomponent polymers such as multilayered thin films, phase separated blends, and microphase separated block copolymers.

## **"ENVIRONMENTAL EFFECTS ON BIOMOLECULAR ACTIVITY"**

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### **ABSTRACT**

Nature pressures species to diversify through a process of adaptation and selection termed evolution. Evolution and perhaps the process of natural selection comprise a number of events that are actively being investigated within natural environments. Over the past ten years, accelerated rates of evolution have been achieved in laboratory environments to produce microorganisms and enzymes with tunable activity. Two of these approaches are being investigated in our laboratory. Forced Molecular Evolution (FME) has been used to facilitate the adaptation of a consortium of microorganisms now capable of hydrolyzing nerve agent analogues or organophosphonothiolate compounds (1). Through the application of a long-term continuous culture and a gradually changing environment of chemical growth substrates over time a new hydrolytic activity has been developed within the consortium (2). The second approach, directed evolution, is defined as "harnessing Darwinian natural adaptation on a molecular scale so that macromolecules can be pushed to evolve toward any functional goal (3)." Briefly, random peptide libraries are generated by combinatorial means and screened. This cycle of random mutagenesis and screening is repeated until a biomolecule with the desired properties is identified. We are using directed evolution to develop novel pathogen binding peptides with improved performance and discrimination relative to existing antibody and gene probe reagents. In addition, several examples of newly evolved enzymes with potential industrial applications will also be discussed.

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## SYNTHETIC MOBILE STRUCTURES ON SURFACES

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Surface structures with attached dipolar rotors mounted with their axes normal to the surface and capable of responding to an outside electric field promise to have strongly non-linear dielectric properties. We report a molecular dynamics computer simulation of the response of a single strongly dipolar rotor to rotating electric field, using the Universal Force Field of Rappé and Goddard.<sup>1</sup> We discuss the effects of factors such as field strength and frequency, temperature, and rotational barrier, and interpret the results in terms of a simplified classical rotor model with friction. Three rotational regimes are identified, in which the system acts as a synchronous rotor, an asynchronous rotor, and a perturbed Brownian rotor. We describe efforts to fabricate quartz surfaces covered with an irregular array of dipolar rotors at various degrees of dilution, and to examine their response. We also report the state of our synthetic approach to surface-mounted and free-standing regular 2-D square-grid polymers for mounting the rotors in a regular array with a controlled rotor-to-rotor separation. In this synthesis, star-shaped monomers are forced to adhere to a liquid-liquid interface by attachment of tentacles carrying suitable substituents, and a cross-linking agent is added to one of the liquids. The current issues are the size and regularity of the resulting square-grid polymer domains. Finally, some attention will be given to the possibility of using chiral propeller-shaped dipolar rotors and driving them by a transverse flow of gas.<sup>2</sup>

*Acknowledgment:* This project has been supported by NSF and USARO.

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# Molecular Assembly for Intelligent Materials

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The manifestation of the intelligent functions is characterized by the information processing functions concerned with the systematic cooperation of multiple functions such as the ability to feedback, standby, recognition/discrimination and information integration. More basic intelligent functions include time-responsiveness, environment-responsiveness and homeostasis. Although most definitions of these functions are similar to the action of biological functions, they are not always expressed in biological and medical terms, but more often in terms indicative of biological actions.

Materials may respond to environmental conditions intelligently by sensing changes in environmental conditions, the processing the sensing information and finally actuating the environment to keep homeostasis, for example. In other words, multiple functions should be systematically coordinated. These multiple functions are essentially divided into three primitive functions, the sensor function, the processor function including the memory function, and effector (or actuator) function. In most cases, these three elements work in conjunction support functions such as systematic information network and energy conversion/supply function. These functions are based on the physical and chemical structures at the most fundamental level.

In the research and development on intelligent materials, the basic task from the starting point involves making some breakthrough concerning how to create primitive functions from chemical and physical structures, namely molecular and its aggregate structures and how to systematize functions.

In this report, highly functional materials with specially designed molecular assembly would be included in the category of the intelligent materials. The methods to create new molecular assembled states will be presented in related with the functions.



## **Novel Filled Polymeric Structures for Electrical Properties**

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Electrical properties of binary filled polymer mixtures depend strongly on the microstructure. In particular, filler geometry, dispersion state, filler-filler and filler-matrix interactions strongly affect the electrical properties of composite materials. External variables such as temperature and mechanical stretching may also significantly affect the microstructure and thereby the macroscopic conductivity. If there is a simple relationship between electrical conductivity and external variable, the composite has potential applications as a sensor. Several novel polyolefin systems filled with metal and carbon particles were developed and studied to reveal the relationship between microstructure and electrical properties.

Composites that incorporate carbon conductive filler into an ethylene-octene (EO) elastomer matrix were explored to develop new materials suitable for mechanical sensor applications. Comparing three types of fillers (carbon black, low structure carbon black and high structure carbon black), it was found that the composite with high structure carbon black exhibited a combination of properties not generally achievable with this type of filler in the conventional rubber matrixes. Among the most notable features of the EO composites, completely reversible variation of the resistivity up to 20% strain suggested that these materials might be useful as strain gages. The explanation of the unusual properties of EO with high structure carbon black required unique features of both filler and the matrix.

Continuous layer-multiplying coextrusion offers a new approach for processing filled polymers into conducting structures. In this process, filled and unfilled polymers are combined into unique structures with many alternating layers of two or more components. The ability of microlayering to "organize" anisotropic particles was used to obtain metal-filled polypropylene (PP) tape with highly anisotropic electrical properties. Isolation of individual filled layers by alternating filled and unfilled layers resulted in materials with many independent conductive pathways. When the thickness of the filled layers approached the particle thickness, the conductive properties were lost. This behavior was understood by comparing the three-dimensional arrangement of particles in thick conductive layers with the two-dimensional particle layout of thin non-conductive layers.

Interdiffusion of a polymer pair in microlayers was exploited to increase the concentration of conductive particles in one of the components. When microlayers of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) were taken into the melt, greater mobility of linear LLDPE chains compared to branched LDPE chains caused the layer boundary to move in the direction of the more slowly diffusing chains in a manner similar to the Kirkendall effect in metals. This resulted in substantial shrinkage of the LLDPE layers and corresponding thickening of the LDPE layers. Adding a particulate in the LLDPE did not impede the process of interdiffusion in the melt, and the resultant shrinkage served to increase the particle concentration. For example, resistivity of initially nonconductive LLDPE layers containing nickel platelets decreased by 6 orders of magnitude into highly conductive range after shrinkage concentrated the particles.

## Combinatorial Libraries - Tuning of Reversible Macromolecular Systems

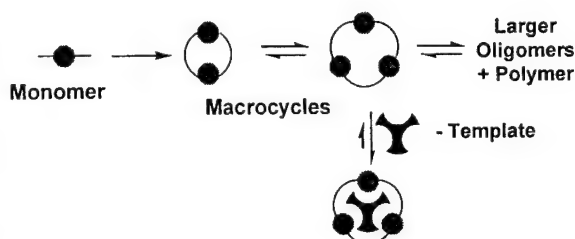
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Thermodynamic control dominates the world of *chemistry beyond the molecule*, allowing access to a wide range of self-assembled macromolecular aggregates, which are formed reversibly. However, on account of the weak non-covalent bonding interactions, such supramolecular aggregates are difficult to characterize and/or utilize in solution. Therefore, the idea of being able to synthesize more robust analogs of these non-covalently bound systems is an appealing one. Reversible (*dynamic*) covalent chemistry can lead to the formation of molecules under thermodynamic control. Initial investigations into the use of dynamic chemistry will be described, focusing on being able to mimic non-covalent supramolecular chemistry, at the covalent level. This talk will concentrate on developments in the areas of dynamic combinatorial chemistry and dynamic interlocked molecules. The potential applications and utilization of reversible chemistry in the area of macromolecules will also be discussed.

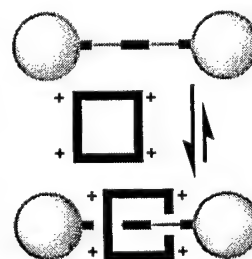
### Dynamic Combinatorial Libraries

A combinatorial library consists of many members ( $M_1 \dots M_n$ ) each of which contains two or more building blocks (*A*, *B*, *C*...) arranged in a particular way. In a traditional combinatorial library the covalent bonds between building blocks are fixed by using irreversible (kinetically-controlled) chemistry during the synthesis, thus precluding postsynthetic interconversion between members. However, in a dynamic combinatorial library the connections between building blocks are reversible and in flux, continuously being formed and broken. This equilibrating behavior means the library, once formed, can still readjust to a perturbation of its environment. For example, if a library of macrocycles is produced, then upon addition of a substrate, macrocycles that are strong binders of the substrate would be stabilized. This template-effect results in the library modifying its distribution, increasing the concentration of macrocycles that are good receptors for the substrate. An investigation into the behavior of reversible (*via* transesterification) macrocycle formation will be presented, focusing on the effect rigidity has upon the macrocycle distribution.



### Dynamic [2]Rotaxanes

Utilizing the dynamic nature of the imine bond, it is possible to construct dynamic [2]rotaxanes, held together by donor/acceptor interactions, from a preformed macrocycle and a preformed dumbbell under thermodynamic control. These dynamic [2]rotaxanes exhibit reversible supramolecular-like behavior in the presence of an appropriate catalyst. Furthermore, by simple reduction of the imine bonds, it is possible to 'fix' the dynamic [2]rotaxanes.





## Polyelectrolyte Multilayers: New Opportunities for Polymer Thin Films

Michael F. Rubner

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Polyelectrolyte multilayers fabricated from weak polyacids such as poly(acrylic acid) exhibit a number of technologically useful properties related directly to their novel molecular architectures and their response to changes in solution pH. Since the degree of ionization of the polyacid chains can be controllably varied via pH changes, it is possible to utilize these multilayer thin films as nanoreactors for inorganic and metallic particles or transform them into uniform, large area microporous thin films. In the former case, the acid groups are used to sequester inorganic ions that are subsequently converted into nanoparticles. Spatial control at the nano-scale level over the location of the particles can be achieved with the use of bilayer combinations that are not able to bind inorganic ions. In the latter case, conditioning specific weak polyacid-based multilayer assemblies in low pH solutions results in a phase separation process that creates uniform microporous thin films that may find utility as membranes, low dielectric materials or biomaterial interfaces. The layer-by-layer deposition process used to fabricate these multilayers also provides control over the molecular-level blending of a polycation/polyanion complex thereby giving nanoscale control over electrical and optical properties. We have used this approach, for example, to dramatically improve the performance of light emitting devices based on conjugated polymers and Ru(II) complexes. Details concerning the fabrication and properties of these new polyelectrolyte multilayer thin films will be described.

# **Charge Injection and Transport in Organic Light-Emitting Diodes**

**J. Campbell Scott**

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Organic light emitting diodes (OLEDs) have been identified by scientists, technologists and industry analysts as a strong contender for the burgeoning flat-panel display market. They exhibit luminances, power efficiencies, color gamuts and lifetimes that are competitive with other technologies, and in addition can be made in extremely thin, lightweight and even flexible form factors. The basic operating principles of OLEDs are well understood, but further enhancement of their performance will depend on our ability to generate accurate, predictive models of the physical processes of device operation. To this end, we and others have been examining the factors which control the injection of charge from the metallic electrodes into the organic layers, the motion of that charge across the layers, and the recombination of electrons and holes to create the emissive exciton species. Injection is governed by the energy level differences (the "barriers") between the Fermi energy of the anode and the organic HOMO for hole injection, or the cathode and the LUMO for electrons. Attempts to measure this energy barrier reveal the existence of interfacial dipole layers whose origin is not yet fully understood. The situation is further complicated by the disordered nature of the active organic layers which introduces inhomogeneity in the energy level structure and drastically affects the injection and transport processes. In this talk I will survey experimental results pertinent charge motion and discuss the extent to which they provide a complete model of device behavior.

# **Oriented Conjugated Polymers: Processing and Application in Display Devices**

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A brief overview of processing routes that allow to render semiconducting conjugated polymers into highly oriented structures is presented. Particular emphasis is devoted to the processing of blends of conjugated polymers or oligomers and 'inert' carrier polymers. The physicochemical aspects of these processing schemes are discussed based on selected examples. In view of the potential use as photoluminescent (PL) polarizer in liquid-crystal displays, the anisotropic photophysical properties of oriented PL materials have received our special attention. These materials exhibit highly polarized absorption and emission properties and, thus, efficiently combine two separate features: the polarization of light and the generation of a specific color. A polarizing energy transfer process can be used to produce PL polarizers of ultimate efficiency. The effect is displayed by materials which comprise a randomly oriented sensitizer that maximally harvests optical energy by isotropic absorption, efficiently transfers the energy to a uniaxially oriented, photoluminescent polymer which subsequently emits linearly polarized light. A systematic investigation of this effect is presented for a number of materials, and important aspects regarding the optimization of these systems are discussed. Finally, we also report our efforts regarding the application of a family of highly luminescent, rigid-rod poly(*p*-phenylene ethynylene) derivatives as the emitting layer in light-emitting diodes.

## STRUCTURE / PROPERTY RELATIONSHIPS IN BIODEGRADABLE POLY[3-HYDROXYALKANOATE] COPOLYMERS

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The successful chemical synthesis of high  $M_w$ , semicrystalline random copolymers of almost fully isotactic poly(3-hydroxybutyrate-co-3-hydroxyalkanoates) has been previously demonstrated<sup>1</sup>. Bacterial synthesis of such isotactic aliphatic polyesters is also becoming possible through fermentation by either the discovery of new microorganisms or via genetic engineering routes<sup>2</sup>. The degree of crystallinity of these new biodegradable thermoplastic PHA's may be controlled by the random incorporation of "defects" such as branching along the chain, much like in LLDPE. A comprehensive study of the structure-property relationships of these materials over a wide range of crystallinity or composition becomes possible, and parallels previous similar studies on polyolefins<sup>3</sup>.

This presentation will introduce this new class of thermoplastic polyesters and describe some of their specific physico-chemical characteristics, including aspects of their biodegradation. An attempt to classify these materials on the basis of their mechanical properties will be presented, which incorporates certain unusual findings about their deformation behavior. Efforts to describe certain aspects of the deformation of PHA's using established models (such as the cross-link/slip-link model<sup>4</sup>) are also being pursued.

<sup>1</sup> L.A. Schechtman and J.J. Kemper, *Polym. Prepr.* (1999), **40**(1), 508;

<sup>2</sup> H. Matsusaki, H. Abe and Y. Doi, submitted to *Biomacromolecules*;

<sup>3</sup> S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner and E. Baer, *J. Polym. Sci., Part B: Polym. Phys.*, **34**, 1301 (1996);

<sup>4</sup> S. Bensason, E.V. Stepanov, S. Chum, A. Hiltner and E. Baer, *Macromolecules*, **30**, 2436 (1997);

## AFM imaging of polymers at different temperatures

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Visualization of morphology and nanostructure of polymers with atomic force microscopy (AFM) substantially complements other microscopic and diffraction techniques in analysis of polymeric materials. Several examples, which include visualization of single macromolecules, grain or block nanostructure of typical crystalline polymers (polyethylene, polypropylene, polyketone, etc.) and monitoring of structural changes at thermal phase transitions, will be presented. AFM images reveal a length and shape of single macromolecules, their packing motifs in single and top layers. High-resolution imaging on sub-micron scale allows examination of lamellar and grain nanostructure in various polymer samples. Recent developments in the AFM characterization of polymers involved measurements at different temperatures. Such studies, which were performed for several polymers, provided real-space visualization of structural changes during their melting and crystallization, as well as kinetic estimates of the spherulites' growth. Further trends in AFM of polymers will be also discussed.

## RIGID-ROD BIBENZOATE MONOMERS AND POLYESTERS

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### ABSTRACT

The commercial development of rigid-rod polyesters based on 4,4-bibenzoic acid has been precluded by the high (\$3/lb) projected selling price for the monomer. Development of a process capable of producing either the 4,4' or the 3,4' isomer of bibenzoic acid *selectively*, at less than \$1/lb, will be reported. Differences in the thermal behaviors of polyesters based on 4,4'-and 3,4'-bibenzoate will also be discussed.